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## Functionalised Carbon Nanoparticles, Blacks and Soots as Electron Transfer Building Blocks and Conduits

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Focus Review

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## Abstract

Functionalised carbon nanoparticles or blacks have promise as novel active high-surface area electrode materials, as “conduits” for electrons to enzymes or “connections” through lipid films, or as nano-building blocks in electroanalysis. With previous applications of “bare nano-blacks” and composites mainly in electrochemical charge storage and as substrates in fuel cell devices, the full range of benefits of bare and functionalised carbon nanoparticles in assemblies and composite (bio-)electrodes is still emerging. Carbon nanoparticles are readily surface-modified, functionalised, embedded or assembled into nanostructures, employed in bio-electrochemical systems, and incorporated into novel electrochemical sensing devices. This focus review summarises aspects of a rapidly growing field and some of the recent developments in carbon nanoparticle functionalisation with potential application in (bio)-electrochemical, photo-electrochemical, and electroanalytical processes.

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**Key Words:** voltammetry, nano-onions, c-dots, layer-by-layer, fluorescence, biosensor.

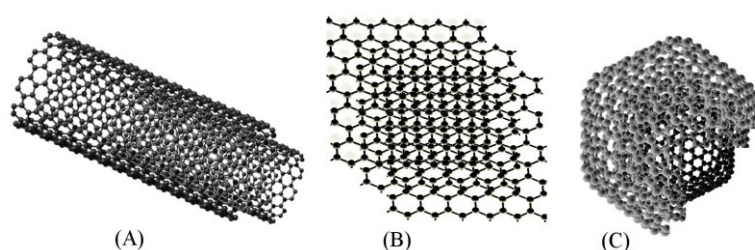
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## 1. Introduction to Carbon Nanoparticles, Blacks and Soots

Carbon blacks<sup>[1]</sup> and in particular acetylene black have been extensively studied by electrochemical means<sup>[2]</sup> and employed in many areas such as energy storage<sup>[3]</sup> and catalysis. Typical particle sizes for commercial blacks are 1 to 50 nm in diameter with a high surface area accessible for chemical functionalization and ideal for effective interaction with redox active species. Although these materials are structurally less well-defined in comparison to carbon nano-tubes,<sup>[4]</sup> nano-onions,<sup>[5]</sup> or graphene materials,<sup>[6,7]</sup> they offer many opportunities for new devices and technologies, for example, nano-carbon-based sensors<sup>[8]</sup> and nano-composites with imprinted polymers applied in shape-selective sensing.<sup>[9]</sup> Carbon blacks in batteries and energy storage are important<sup>[10]</sup> and “metal-free” battery systems have been reviewed.<sup>[11]</sup> In fuel cells and in electrocatalysis, the correct choice of the nano-carbon substrate is important and “carbon substrate effects” have been reviewed.<sup>[12]</sup> The application of Pt-carbon nano-material composites in CO<sub>2</sub> reducing driven fuel cells<sup>[13]</sup> has been reported. In fuel cells, carbon blacks allow gas flow into reactive catalyst layers and optimisation is required to maintain stable operation conditions. The oxidation of carbon blacks during operation of anodes (and when exposed to peroxides at cathodes) poses a problem that has been discussed by Dowlapalli et al.<sup>[14]</sup> A comprehensive review about carbon powder and nano-carbon applications in power electrochemistry has appeared<sup>[15]</sup> with a systematic investigation of material properties and important parameters such as purity, structure, texture, and particle size. Also, the formation and properties of carbon black - metal oxide nano-composites has been reviewed<sup>[16]</sup> with detailed information about electrical (sensing) and mechanical properties.

Recent interest in structurally more defined nano-carbon nano-materials was stimulated by the discovery of carbon nanotubes (CNTs) by Iijima in 1991<sup>[17]</sup> and graphene by Novoselov and Geim in 2004<sup>[6]</sup> (see Figure 1). Multi-shelled carbon nano-onions (structurally similar to very short multi-walled nano-tubes) have been obtained, for example, from nano-diamond at high graphitization temperature (2000 °C) and suggested for applications in energy storage.<sup>[18]</sup>



**Figure 1.** Schematic drawings of multi-layered nanostructured carbon materials for the case of (A) nanotubes, (B) nano-graphenes, and (C) carbon nano-onions.

On the other hand, structurally less-defined carbon nanoparticles (CNPs) have been applied for a considerable time with some evidence for use even as a pigment for prehistoric wall art,<sup>[19]</sup> and as a key component in the rubber and tyre industries as fillers to extend the lifetime of polymers.<sup>[20,21]</sup> CNPs have received significant attention as they exhibit many unique functions and characteristics that are attributable to their nano-scale dimensions, typically 1 nm - 100 nm in diameter.<sup>[22,23]</sup> Nano-carbons, including CNPs, generally exhibit extremely high surface areas, high conductivity, and a multitude of reactive surface and adsorption sites.<sup>[24]</sup> CNPs may be considered more economical than other nano-carbons, as they are produced commercially in bulk quantities and also often formed as waste by-products during the formation of other nano-materials such as CNTs.<sup>[25]</sup> The term CNPs encompasses

a variety of nano-materials including carbon blacks, soots, carbon dots (“c-dots”<sup>[26]</sup>), and novel core-shell nano-carbons.<sup>[27]</sup>

One of the main commercial uses for carbon black is as a pigment or as an additive to polymeric materials. The stabilising effects of carbon nanoparticles on rubber lifetimes arise for a number of different reasons. The surface groups of the nano-materials are known to interact with polar rubber materials, which result in reinforcement of the polymer.<sup>[28]</sup> These surface groups are typically carboxylic acids, phenol, quinone, and lactone groups, which attach to the graphitic edge planes of carbon nanoparticles. Pěna *et al.* investigated the behaviour of carbon blacks and discovered that the efficiency of the nanoparticles on prolonging the lifetime of the rubbers was increased with increasing concentration and decreasing particle size.<sup>[29]</sup> It was realised that carbon black pigments were effective as singlet-state and triplet-state quenchers of carbonyl chromophores present in low density polyethylene.<sup>[30]</sup> Pěna *et al.* further investigated the adsorption of antioxidants and specific light stabilisers onto the surface of the carbon black pigments by flow micro-calorimetry. They found that the adsorption activity is related to the number of active functional groups on the surface of the carbon black material. It was also clear that carbon nanoparticles with highly oxidised surfaces showed a greater adsorption affinity for the stabilisers. The surface functionality of the carbon black greatly affected the stabilisation properties of the additives.<sup>[31,32]</sup> There are a number of commercially available carbon black nanoparticles, which have a diverse array of surface functionalities. One of the most frequently applied carbon blacks is Vulcan<sup>TM</sup> XC-72R (Cabot Corp.).<sup>[33]</sup> This material has been particularly important for the development of electro-active catalyst composites for fuel cells because of its high surface area and good electrical

conductivity. The surface of Vulcan<sup>TM</sup> is furnished with quinone moieties to make it an important precursor material for surface modifications. Different oxidation conditions result in Vulcan<sup>TM</sup> nanoparticles with functional surface groups, such as carboxyl groups, lactones, anhydrides, phenols, or additional quinone groups.<sup>[34,35]</sup>

## **2. Carbon Nanoparticle Formation, Modification, and Characterization**

### ***2.1. Acetylene Blacks***

Acetylene blacks may be considered as a prototype of carbon blacks, which can be obtained via thermal decomposition of acetylene (into carbon and hydrogen) to give a very pure form of nano-carbon.<sup>[36]</sup> When obtained under mildly oxidising conditions, the products become a variety of the broader family of combustion synthesis nano-materials (*vide infra*). Both pure acetylene blacks and doped acetylene blacks<sup>[37]</sup> have been employed extensively in particular in fuel cell systems<sup>[38]</sup> and in novel battery systems.<sup>[39]</sup> Not surprisingly, acetylene blacks offer a versatile electrode component also for electroanalytical applications. Composites of acetylene black, for example with poly-ethylene-glycol and cytochrome P450 enzymes have been employed directly in electroanalysis.<sup>[40]</sup> Nano-composites with modified chitosan have been employed for the detection of nitrophenols.<sup>[41]</sup> Acetylene black “solubilised” with dihexadecyl hydrogen phosphate has been employed for the determination of chrysophanol.<sup>[42]</sup> The detection of insulin was reported on acetylene black paste electrodes.<sup>[43]</sup> In all cases, the high surface area of these materials is crucial in

improving the performance of devices.

## **2.2. Combustion Synthesis Blacks and Soots**

For many years, the formation of carbon nanoparticles has been achieved by either the pyrolysis (pre-mixture of fuel and air) or incomplete combustion (where oxygen diffuses into a gaseous fuel) of hydrocarbons.<sup>[44]</sup> Polymer precursors are commonly employed for pyrolysis methodologies, because the fuel should be thermally stable and able to form useful carbon residues following the high-temperature processing.<sup>[45]</sup> The carbonisation process can occur through a number of different techniques. Most common are premixed flame methods, in which the oxidiser is mixed with the hydrocarbon fuel in advance ensuring that all reactants are readily available.<sup>[46]</sup> Laminar diffusion flames,<sup>[47]</sup> turbulent flames,<sup>[48]</sup> and other flame methods have been utilised. The incomplete combustion of hydrocarbons leads to the formation of condensed carbonaceous particles (soot) in the nanometre diameter range, and these combustion-generated materials tend to exhibit the transport and surface related phenomena associated with nanoparticles in addition to maintaining molecular features such as chemical reactivity.<sup>[49]</sup> These materials, often called carbon blacks, form *via* condensed-phase carbonization. In contrast, the combustion of hydrocarbons to form carbonaceous nano-materials may also follow an entropically favourable pyrolysis mechanism due to initial gas production. The most common intermediate in hydrocarbon pyrolysis is acetylene (*vide supra*). Although the formation of acetylene from saturated hydrocarbons is endothermic, the process is associated with a large release of H<sub>2</sub> gas, which significantly increases the entropy of the process. Berthelot<sup>[50]</sup> suggested that acetylene was a necessary intermediate for solid carbon



formation, as did Porter who explained that the simultaneous polymerization and hydrogenation of acetylene was essential to carbon nanoparticle formation.<sup>[44,51]</sup>

### ***2.3. Hydrothermal Synthesis of Blacks and “C-Dots”***

The hydrothermal method of processing materials at high temperature/pressure originally described the way in which water changed the Earth to form rocks and minerals at high temperatures and pressures. More recently, hydrothermal processing was defined as any chemical reaction in the presence of a solvent (usually aqueous solvents, as non-aqueous processing is often termed solvothermal) at elevated temperatures and pressures, within a closed system.<sup>[52]</sup> Hydrothermal carbonisation is a rapidly expanding field<sup>[53,54]</sup> and utilises hydrothermal conditions to synthesise carbonaceous materials from low cost and widely available precursors such as carbohydrates,<sup>[55,56]</sup> polymers<sup>[57]</sup> and biomass,<sup>[58,59]</sup> to name a few.<sup>[60]</sup> The hydrothermal carbonisation process has been advanced considerably and is now utilised for the synthesis of a wide range of new solid materials with control over their shape, size, and functionality.<sup>[61]</sup> Hydrothermal carbonisation offers advantages such as simplicity and cost effectiveness, better control over nucleation processes, greater dispersion and rates of reaction, as well as being more environmentally friendly, as the process is carried out in aqueous media in a closed vessel.<sup>[62]</sup> The hydrothermal process is usually performed at temperatures between 160 °C and 200 °C. Initially, the starting material undergoes dehydration before condensation, polymerisation, and core-aromatisation occur; finally colloidal carbon nanoparticles are formed usually with a polymer shell that needs to be removed for electrochemical applications. In contrast to the hydrothermal process, the solvothermal or molten salt-based synthesis

of pure carbon materials (nano-flakes) has been reported to directly give highly electrochemically active materials.<sup>[63]</sup>

Compared to the combustion methods, hydrothermal carbonisation generally results in carbon nanoparticles that have a much more diverse surface functionality. In fact, the resulting surface can be chemically very similar to the starting material (due to incomplete surface carbonisation) and therefore the resultant carbon nanoparticles can be modelled on the precursor material that is used to create them. Due to incomplete surface carbonisation, colloidal “c-dot” products with intriguing spectroscopic and fluorescent properties are often obtained.<sup>[64]</sup>

The hydrothermal transformation of carbon nanoparticles of approximately 5 nm diameter from natural gas soot<sup>[65]</sup> into photo-luminescent particles was reported by Chen and coworkers.<sup>[66]</sup> The transformation of non-radiative surface functional groups (e.g. quinones) under mild hydrothermal conditions was reported to be essential for improved photochemical performance.

#### ***2.4. Carbon Nano-Onion Blacks***

A more recent and particularly exciting development in carbon nanoparticle materials is the formation and application of carbon “nano-onions”.<sup>[67,68]</sup> A clean production of these onion structured nano-carbons is possible via thermolysis of nano-diamond,<sup>[69,70]</sup> but also via flame,<sup>[71]</sup> arc discharge,<sup>[72]</sup> chemical reactions,<sup>[73]</sup> laser ablation

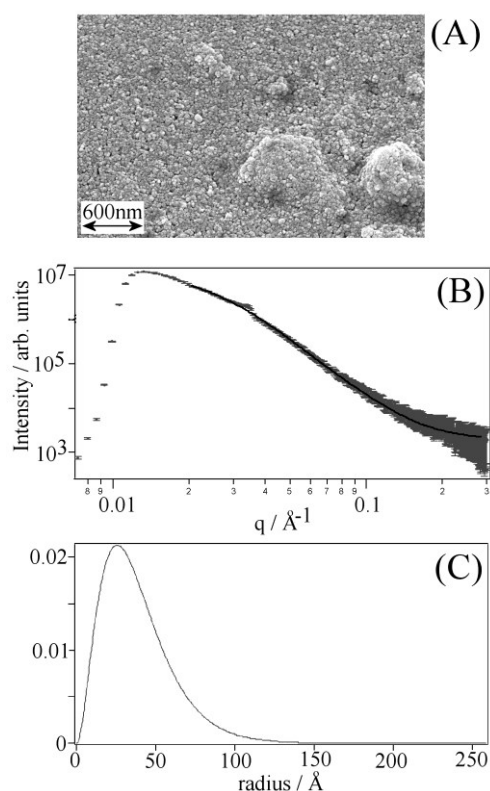
methods,<sup>[74]</sup> and castor oil combustion methods.<sup>[75]</sup> Solvent-soluble nano-onions were recently obtained by Echegoyen and coworkers in a hexadecyl surface modification reaction.<sup>[76]</sup>

## **2.5. Surface Modification of Carbon Nanoparticles**

A review of the surface chemistry of carbon blacks has been provided by Boehm.<sup>[77]</sup> More recently, chemical modification of carbon surfaces was reviewed by Wildgoose.<sup>[78]</sup> A plethora of carbon surface functionalisation methods are available and have been employed in the surface modification of carbon nanoparticles. Downard and coworkers demonstrated siloxane immobilisation followed by “click” chemical binding<sup>[79]</sup> and developed diazonium coupling chemistry.<sup>[80,81]</sup> Diazonium coupling chemistry<sup>[82]</sup> linking phenylsulfonate functional groups is employed today on industrial scale for the formation of negatively charged water-soluble carbon nanoparticles such as Cabot’s pigment Emperor 2000<sup>TM</sup>. New covalent modification reactions including intercalation and tethering of nitroanilines have been developed by Compton’s group.<sup>[83]</sup> Direct surface modification with palladium nanoparticles has been reported by the same group.<sup>[84]</sup> Chen and coworkers synthesised ferrocene-functionalised carbon nanoparticles<sup>[85]</sup> employing a diazonium coupling reaction. For phenylsulfonate-modified carbon nanoparticles, the transformation to sulphonamide<sup>[86]</sup> has been proposed by Bull and coworkers as a versatile route to a variety of hydrophilic or hydrophobic, positive or negative, as well as redox-active nano-carbon materials (*vide infra*).

## 2.6. Characterisation of Carbon Nanoparticles

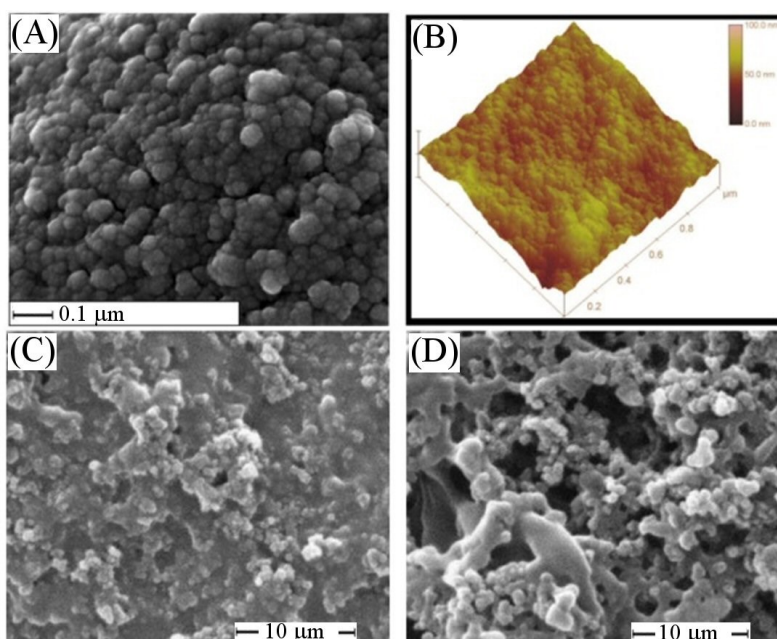
High surface area carbon nano-materials, in particular carbon blacks<sup>[87]</sup> such as Emperor 2000<sup>TM</sup>, exhibit high gas binding ability (the dry carbon nanoparticle powder gives a BET isotherm<sup>[88]</sup> area of  $346 \text{ m}^2\text{g}^{-1}$ ). Scanning electron micrographs (see Figure 2A) of the carbon nanoparticle material confirm a particle size in the order of 5 nm radius and, small-angle X-ray scattering experiments (carried out with a colloidal solution of 6% (w/v) carbon nanoparticles in water, see Figure 2B) suggest a mean particle radius 3.8 nm obtained by fitting the model of spherical particles.<sup>[88]</sup> Figure 2C represents a measure of the range of particle sizes encountered in this material.



**Figure 2.** (A) SEM image of carbon nanoparticles (gold sputter coated prior to imaging). (B) SAXS data (with error bars shown) for a 6% (w/v) carbon nanoparticle solution in water. The black line shows the theoretical fit assuming spherical particles with a mean radius of  $38 \pm 2 \text{ \AA}$  and a poly-dispersity of 0.57. (C) Schultz distribution calculated by fitting SAXS data.<sup>[88]</sup>

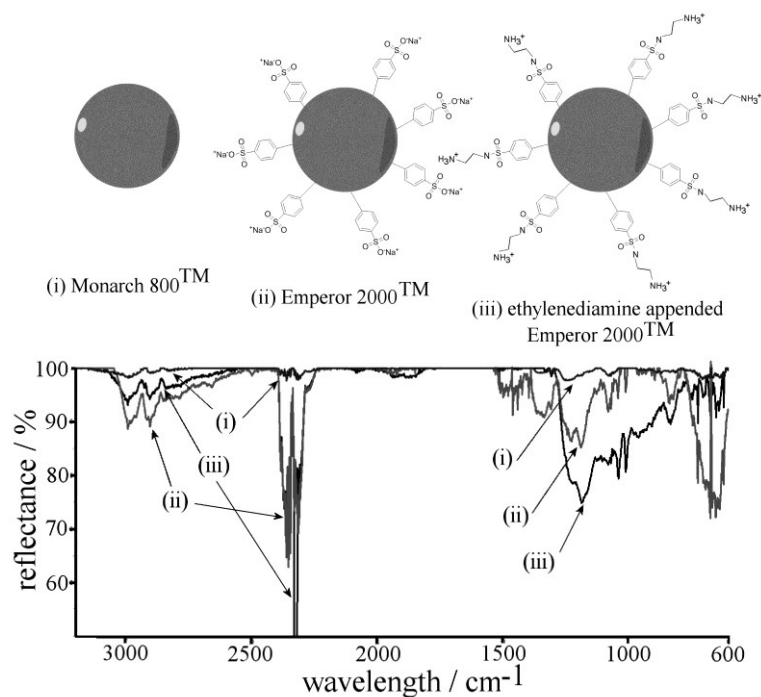
X-ray photoelectron spectroscopy (XPS) is a quantitative characterisation technique that involves the irradiation of the material of interest with an X-ray beam. XPS can be used to study the energy distribution of electrons that are emitted from X-ray-irradiated species.<sup>[89]</sup> XPS data for example for Emperor 2000<sup>TM</sup> and ethylenediamine appended Emperor 2000<sup>TM</sup> have been reported.<sup>[88]</sup>

Szot and co-workers<sup>[90]</sup> employed SEM to show that carbon nanoparticles (CNPs) in a composite with tetramethoxysilane (TMOS)/CNP/laccase form globular structures (see Figure 3) and used AFM to demonstrate that the CNPs were evenly distributed throughout the film. Yu et al.<sup>[91]</sup> have shown how different film growth conditions can lead to different composite morphologies and porosities. In one study, they showed that poly-vinylalcohol (PVA)-CNP films resulted in compacted nanostructured films on glass, whereas when haemoglobin was introduced into the matrix, the films formed a three-dimensional porous film (see Figure 3).



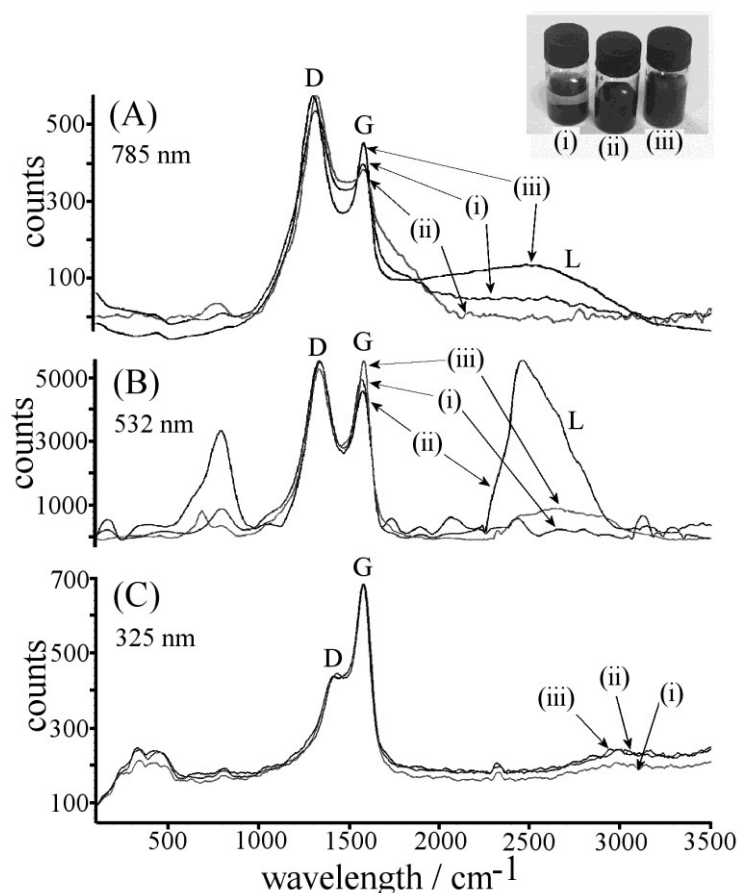
**Figure 3.** (a) SEM image and (b) AFM image of TMOS/CNP/Laccase modified electrode (reproduced from reference.<sup>[90]</sup> SEM images of (c) CNPs/PVA and (d) Hb/CNPs/PVA on glass slides.<sup>[91]</sup>

The surface modification of carbon blacks changes its spectroscopic characteristics, as shown for example in the FTIR reflectance spectra in Figure 4. Three types of carbon black are compared - hydrophobic Monarch 800<sup>TM</sup>, hydrophilic negatively charged Emperor 2000<sup>TM</sup> (both Cabot Ltd.), and hydrophilic positively charged Emperor 2000<sup>TM</sup> with ethylenediamine functionalisation.



**Figure 4.** Drawing of (i) Monarch 800<sup>TM</sup>, (ii) Emperor 2000<sup>TM</sup>, and (iii) ethylenediamine appended Emperor 2000<sup>TM</sup> nanoparticles. DRIFT spectra for carbon nanoblacks measured 1% in KBr pellets under argon.

Reflectance bands in the 2300 cm<sup>-1</sup> region are due to surface bound CO<sub>2</sub>. The surface modified Emperor 2000<sup>TM</sup> shows an increase in signal and the ethylenediamine appended Emperor 2000<sup>TM</sup> exhibits a very strong band (off scale) indicative of surface interaction of the amine with atmospheric CO<sub>2</sub>.<sup>92</sup> Bands in the 2700 cm<sup>-1</sup> to 3000 cm<sup>-1</sup> region are likely to correspond to C-H and C-C bands, but may also contain surface C-O contributions. The 1330 cm<sup>-1</sup> and 1150 cm<sup>-1</sup> regions are associated with S-O bands with S-N expected at about 905 cm<sup>-1</sup>.<sup>[93]</sup> Characteristic Raman spectra for three laser wavelengths, 785 nm, 532 nm, and 325 nm, are summarised in Figure 5.



**Figure 5.** Raman spectra (Renishaw InVia Raman Microprobe) for (i) Monarch 800<sup>TM</sup>, (ii) Emperor 2000<sup>TM</sup>, and (iii) ethylenediamine appended Emperor 2000<sup>TM</sup> nanoparticles (A) at 785 nm, (B) at 532 nm, and (C) at 325 nm laser wavelength. Inset: photograph of aqueous suspensions of the three nanocarbon materials.

Characteristic D and G bands reflect disordered amorphous ( $sp^3$ ) and graphitic ( $sp^2$ ) carbon components.<sup>[94]</sup> Under UV excitation (Figure 4C) there is very little difference in the three carbon materials with the bulk carbon dominating the spectral response. However, in both green and red laser light, a systematic intensity change in the G peak is observed linked possibly to surface charge. Very interesting are the weak luminescence features at ca. 2500  $cm^{-1}$  (indicated “L”), which must be attributed here to surface functional groups modifying the photochemical properties (e.g. suppressing the quenching effects of surface quinones). These processes are novel and largely



unexplored. Future applications of these bands could be in analytical detection for example of gases. When carefully oxidising Vulcan XC-72 carbon black, Yongquiang Dong et al. have observed the formation of highly fluorescent single- and multi-layer graphene nano-dots with potential for application also in optoelectronic devices.<sup>[95]</sup>

Characterisation by optical imaging at solid liquid interfaces of carbon black films has been reported by Fletcher and coworkers.<sup>[96]</sup> During these investigations, carbon black particles were deposited onto cellulose-coated glass slides from a water suspension. This enabled the extinction coefficient of a carbon black to be obtained as  $1.6 \times 10^6 \text{ m}^{-1}$ . Absorbance imaging was used to determine both the absorbance and the film thickness at liquid|liquid emulsion drop surfaces. This technique proved to be a relatively straight forward method to characterise carbon films on both solid and liquid interfaces, which clearly demonstrated the tendency of commercially available Emperor 2000<sup>TM</sup> carbon nanoparticles to form interfacial aggregates. Optical properties of carbon nanoparticles are linked to applications as pigments, but also as carbon-dots in fluorescent markers or “c-dots” with low toxicity.<sup>[97]</sup> Fluorescence of carbon nanoparticles could lead to interesting new applications in particular for well-defined and surface functionalised nano-materials e.g. in bio-imaging.<sup>[98,99]</sup>

### 3. Electrode Surfaces Modified with Carbon Nanoparticle Blacks

#### 3.1. Applications of “Bare” Carbon Nanoparticles

In analytical applications, the high surface area of nano-carbons can be beneficial for the accumulation of hydrophobic analyte molecules. For example, carbon blacks directly immobilised on electrode surfaces can be used to enhance electroanalytical detection of nicotine.<sup>[100]</sup> Also the adsorption of fluorescein onto carbon black has been employed in analytical methods.<sup>[101]</sup> Deposition of carbon black is readily achieved by solvent evaporation, for example from a toluene suspension. Ink-jet deposition of thin films for supercapacitor applications have been reported.<sup>[102]</sup> The hydrophobic surface of as-synthesised carbon blacks offers a high surface area and good binding to hydrophobic analytes. With palladium immobilisation directly into the high surface area hydrophobic substrate, effective electroanalytical detection of hydrazine was possible.<sup>[103]</sup> The detection of nitrate and nitrite on carbon black electrodes has been reported.<sup>[104]</sup> However, in a recent report comparing the electrochemical characteristics of non-functionalised carbon nanoparticles with those of bamboo-type carbon nanotubes, the latter were shown to be more effective.<sup>[105]</sup>

In fuel cell catalysis,<sup>[106]</sup> Vulcan<sup>TM</sup> carbon blacks have been important in the development of platinum-supported electrocatalysts. A common preparation for such catalysts is through the incipient wetness impregnation method.<sup>[107]</sup> The electrocatalytic activity of such carbon-based catalysts can be tuned by adjusting the surface functionalities and subsequently the catalyst morphology.<sup>[108]</sup> The electron transfer in Pt/Vulcan<sup>TM</sup> electrodes has been suggested to occur through the oxygen

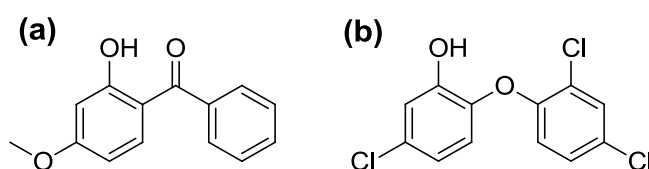
atoms that are located at the surface of the support; therefore, the metal/support interaction is important, and this can be altered by surface modifications on the Vulcan<sup>TM</sup> carbon material, which will result in more efficient functional groups and chemical linkages at the Pt/C surface as well as increasing the surface area.<sup>[109]</sup> Hence, the electrocatalytic activity for such carbonaceous materials can be adjusted by changing the morphology through the surface functionality.

### ***3.2. Applications of Surface-Modified Carbon Nanoparticles***

Surface-modified carbon blacks are of considerable commercial importance, for example the Emperor 2000<sup>TM</sup> from Cabot Corporation. These nanoparticles are prepared from a carbon black precursor by covalent attachment of phenylsulfonate groups. These carbon nanoparticles with diameters of typically 8 to 18 nm are produced via diazonium chemistry.<sup>[110]</sup> Emperor 2000<sup>TM</sup> nanoparticles provide an excellent starting material for covalent attachment of molecules, physisorption, or “hydrothermal wrapping” techniques<sup>[111]</sup> to deliver functionalised nano-core-shell materials (*vide infra*).

Functionalised carbon nanoparticles have a number of potential applications as electrochemical substrates and probes. Modifying electrodes with specifically functionalised CNPs can result in highly sensitive redox sensors for a number of targets. One of such application is for the detection of pollutants in the environment.<sup>[112]</sup> Of recent interest is the analysis of personal care product and

pharmaceutical ingredients to ensure the prevention of concentrations building to harmful levels.<sup>[113]</sup> Vidal and collaborators used Emperor 2000™ CNPs to create modified electrodes for the detection of two common ingredients in personal care products; triclosan – a common ingredient in consumer disinfectants,<sup>[114,115]</sup> deodorants and medical creams, and benzophenone-3 – a UV filter present in many sunscreens and cosmetics (Figure 6).<sup>[116]</sup> Both compounds are found in common household products and can have a detrimental effect on the environment; this can occur through transfer into the wastewater system. Both triclosan and benzophenone-3 are low toxicity compounds; however, under certain conditions photo-degradation can occur to produce derivatives, which may impact negatively the environment.

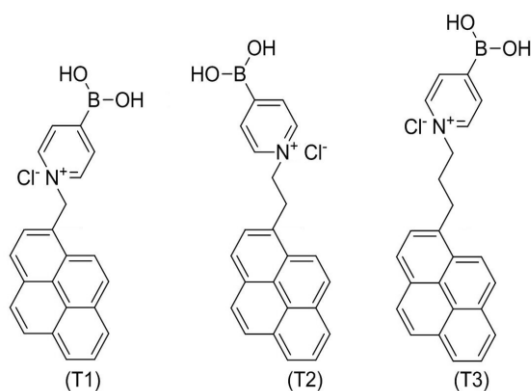


**Figure 6.** Chemical structures of (a) benzophenone-3 and (b) triclosan

In the experiments by Vidal and co-workers<sup>[114]</sup>, the CNPs acted for two purposes, the first was to extract the desired analyte from the sample and the second was to allow for voltammetric investigation. The analytes readily adsorbed to the anionic surface of the CNPs and the modified CNPs were easily dispersed in water allowing for simple deposition of a large surface area sample onto a working electrode providing a probe effective in binding poly-aromatic phenols. This methodology enabled both target molecules to be analysed with a LOD in the micro-molar concentration region.<sup>[114]</sup>

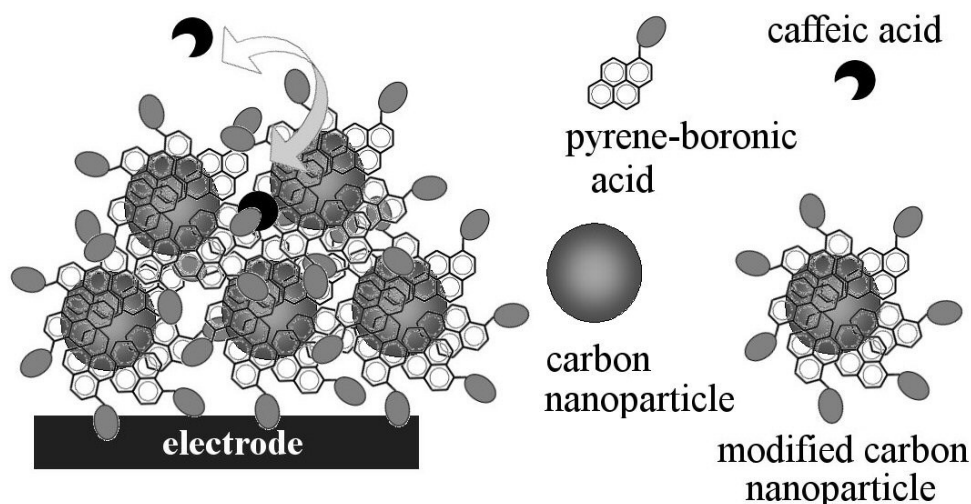
In a recent study by Lawrence et al. cationic pyrene moieties with boronic acid

functionality were shown to self-assemble around commercially available negatively charged phenylsulfonate-coated Emperor 2000<sup>TM</sup> carbon nanoparticles.<sup>[117]</sup> A synthetic route to append pyrene groups onto different boronic acid scaffolds had been developed by Nishimura et al., and these boronic acid-based compounds were then physisorbed onto the surface of carbon nanoparticles through the pyrene functionality (Figure 7).<sup>[118]</sup>



**Figure 7.** Chemical Structure of pyrene-appended boronic acids.<sup>[118]</sup>

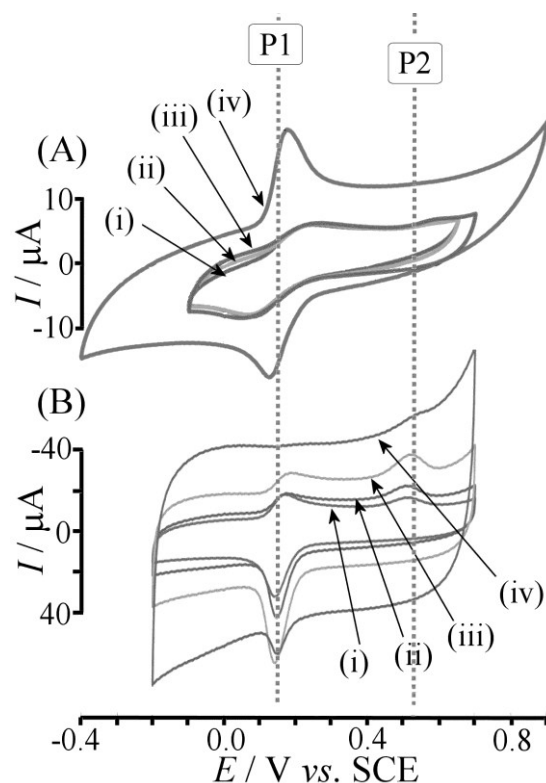
The boronic acid-modified CNPs were insoluble in water and could be readily deposited onto graphite electrodes in a simple drop-casting procedure for use in electroanalytical applications. The terminal boronic acid groups were demonstrated to bind to catecholic caffeic acid when immersed in the electrolyte solution.



**Figure 8.** Illustration of pyrene-appended boronic acid-modified carbon nanoparticle film immobilised onto a graphite electrode.<sup>[117]</sup>

The non-covalently modified electrodes based on nanoparticle aggregates were sensitive to caffeic acid and exhibited Langmuirian binding constants approaching  $10^6 \text{ mol}^{-1} \text{ dm}^3$ . The molecular structure of the pyrene-appended boronic acid was demonstrated to affect the ability of the boronic acid moiety to bind to the caffeic acid. More importantly, the fluxional transformation of the strongly bound (with a high oxidation potential) into the weakly bound (with a lower oxidation potential) form was affected by the change in the length of the carbon linker that was present between the boronic acid and the pyrene moieties. In this investigation, it was highlighted that carbon nanoparticles could provide an ideal substrate material for the self-assembly of pyrene-appended boronic acid receptor molecules (see Figure 9). The CNP-based substrates provided optimised peak responses with high sensitivity to caffeic acid. The two processes observed here are (P1) the oxidation of caffeic acid in solution and (P2) the oxidation of caffeic acid bound to the surface immobilised boronic acid. A wider range of pyrene-appended receptor systems could be bound to

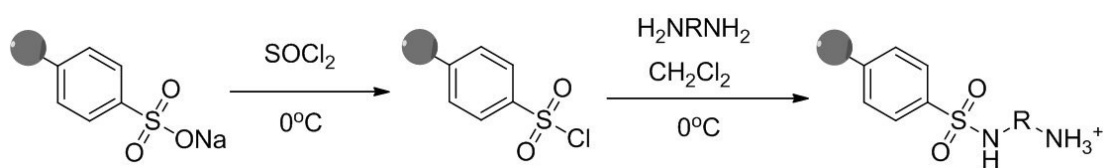
carbon nanoparticles to provide a versatile sensor platform.



**Figure 9.** Cyclic voltammograms (scan rate  $50 \text{ mVs}^{-1}$ ) for (A) 0.17 mM caffeic acid using (i) T1-, (ii) T2-, (iii) T3-modified graphite, and (iv) bare graphite electrodes; and (B) 0.01 mM caffeic acid using graphite electrodes with (i) 3  $\mu\text{g}$ , (ii) 15  $\mu\text{g}$ , (iii) 30  $\mu\text{g}$ , and (iv) 60  $\mu\text{g}$  T1-modified CNPs immersed in 0.1 M pH 7 phosphate buffer solution.<sup>[117]</sup>

Industrially manufactured Emperor 2000<sup>TM</sup> carbon nanoparticles with surface phenylsulfonate groups have been used directly for a number of electrochemical investigations. In 2008 Rassaei et al. formed stable films by using this material in two different ways: (i) drop-cast methods involving solvent evaporation onto glassy carbon electrodes was used<sup>[119]</sup> as well as (ii) electrostatic layer-by-layer deposition.<sup>[120]</sup> The introduction and modification of surface functional groups was explored to improve the chemical selectivity and charge density at the active surface.<sup>[121,122]</sup> Bull and coworkers utilised Emperor 2000<sup>TM</sup> carbon nanoparticles as

the starting material and developed a method to convert the negatively charged sulfonate functionality into a positively charged amine group. This was achieved by converting the sulfonate groups into reactive sulfonyl chloride species by using thionyl chloride, before reaction with a diamine to form a sulfonamide linker and terminal amine units, see Figure 10.<sup>[123]</sup>



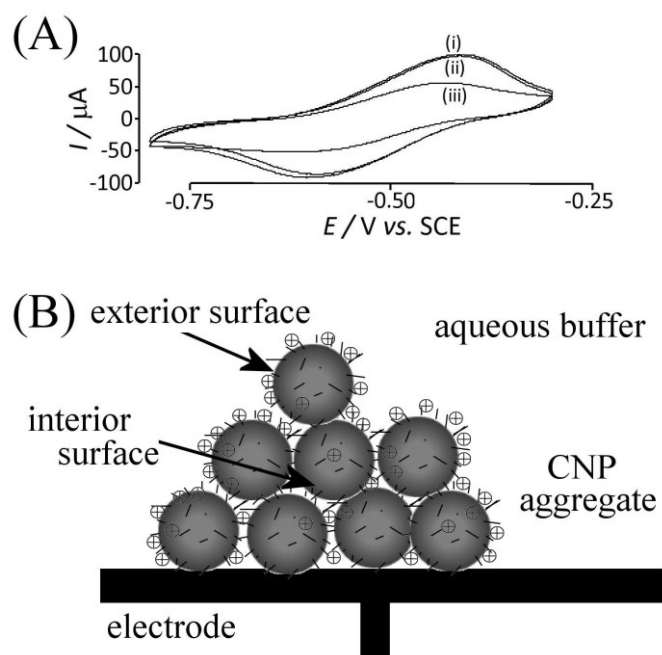
**Figure 10.** Method used by Watkins et al. to convert the surface charge from negative to positive.<sup>[123]</sup>

This work enabled new Emperor 2000<sup>TM</sup>-based nano-composite materials to be formed through the mixing of the starting material and the product as the complementary surface charges assembled into an ionic film. Also, this surface modification method resulted in nanoparticles with amine functionality that could be used for a number of further functionalisations, such as, the covalent attachment of redox active moieties<sup>[124]</sup> or subjecting the particles to amide coupling conditions to append other interesting molecules.<sup>[125]</sup>

Anthraquinone is one such redox active species that has been exploited in this way through covalent attachment to Emperor 2000<sup>TM</sup> carbon nanoparticles.<sup>[119]</sup> Anthraquinone functionality has been important for processes such as pH sensing,<sup>[126,127,128]</sup> catalytic oxygen reduction,<sup>[129,130]</sup> and as a redox mediator.<sup>[131]</sup> In the covalently bound form, anthraquinones provide a reversible redox system that is robust over a large pH range. The anthraquinone moiety has been successfully bound



to Emperor 2000<sup>TM</sup> carbon nanoparticles through ethylene diamine-modified carbon nanoparticles reacting with bromomethyl-anthraquinone.<sup>[132]</sup> The nano-scale dimension of the carbon material leads to increased bulk density of anthraquinones in the pores of the nanoparticle aggregates; this contributes to unique buffer capacity effects. At pH values corresponding to the maximum buffer capacity (i.e., pH 2, 7, and 12 in the case of phosphate buffer), an increased peak current is observed in addition to a lower peak-to-peak separation. The peak shape is also affected by the pore-reactivity, which is influenced by the surface charge of the modified carbon nanoparticles. The secondary amine linker remains protonated (over a large pH window) and introduces a net positive charge onto the particulate surface. When the modified electrode is immersed into a solution of negatively charged BPh<sub>4</sub><sup>-</sup> solution prior to electrochemical investigation, the current values for both the anodic and cathodic peaks are reduced to half of the initial current, as shown in Figure 11. With the hydrophobic anion, anthraquinone moieties that are embedded within the pores are proposed to be less accessible. This demonstrates the ability of modified Emperor 2000<sup>TM</sup> carbon nanoparticles to act as high-density carrier for redox active species.

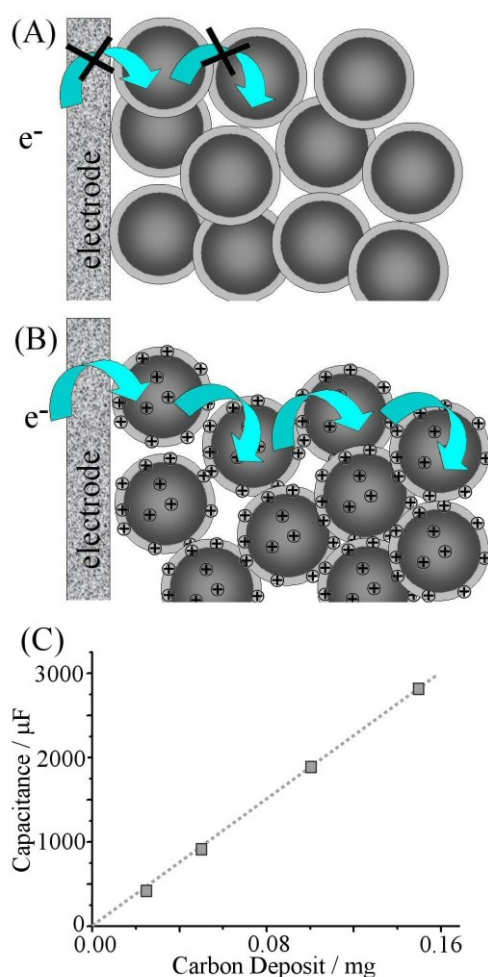


**Figure 11.** (A) CVs (scan rate  $20 \text{ mV s}^{-1}$ ) for anthraquinone-modified carbon nanoparticles ( $10 \text{ mL}$  of  $2 \text{ mg mL}^{-1}$  onto  $3 \text{ mm}$  glassy carbon working electrode) immersed in  $0.1 \text{ M}$  phosphate buffer pH 7 with (i) no pre-treatment (ii) pre-treatment by immersion into  $1 \text{ mM}$   $\text{NBu}_4\text{Cl}$  (iii) pre-treatment by immersion into  $1 \text{ mM}$   $\text{KBPh}_4$  (B) Schematic representation of anthraquinone-modified carbon nanoparticle aggregates when deposited onto the electrode surface where the pore interior and exterior surfaces are indicated.<sup>[132]</sup>

### 3.3. Applications of Surface-Modified Carbon Nanoparticles with “Hydrothermal Wrapping”

Hydrothermal methodologies can be used to convert a variety of precursor materials into carbonaceous nano-materials.<sup>[133]</sup> An important factor in the design of a hydrothermal method is the choice of precursor material as this will have a strong influence on the resulting surface functionality of the carbonised nanomaterial. Starting materials that contain amine groups have been shown to result in nanomaterials with positively charged surface features.<sup>[134,135]</sup> Chitosan has been

subjected to the hydrothermal carbonisation method and was demonstrated to form highly positively charged materials. However, like many materials formed in this way, it was revealed to be completely electrochemically insulating, which could be attributed to a layer of poorly carbonised material that acts as a barrier to electron transfer (see Figure 12).<sup>[136]</sup> This methodology was then applied to chitosan in combination with Emperor 2000™ carbon nanoparticles, known to be highly conducting, and a method for producing core-shell carbon was reported that resulted in an electrically conducting nanomaterial.<sup>[137]</sup>

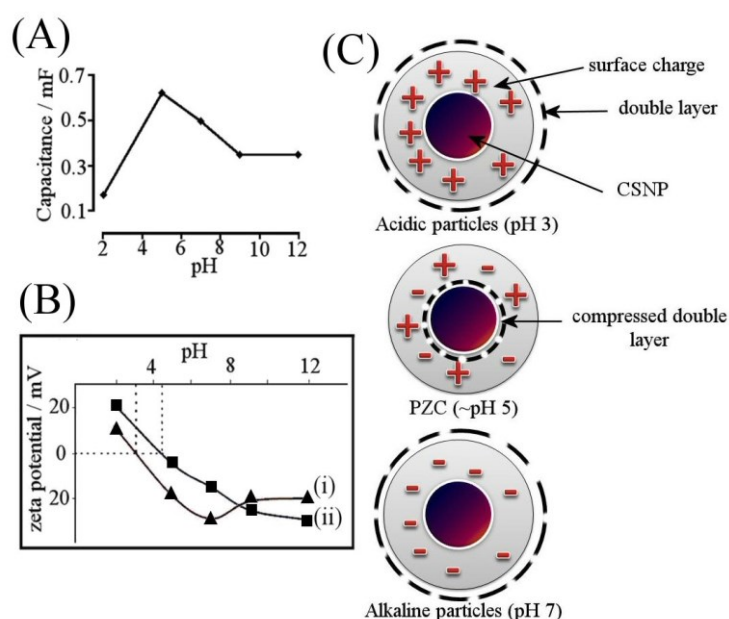


**Figure 12.** Schematic drawing of core-shell carbon nanoparticles with (A) blocking shells (B) electrically conductive shells. (C) Plot of the capacitance (from cyclic voltammetry data - scan rate  $50 \text{ mV s}^{-1}$ ,  $0.1 \text{ M}$  phosphate buffer pH 2) versus the amount of carbon nanoparticle deposit.<sup>[137]</sup>

Control of shell thickness and shell properties are possible and these prove to be crucial factors for accessing interesting functional characteristics. In the case of chitosan-Emperor 2000<sup>TM</sup> core-shell carbon-hydrothermal nanoparticulates, the product was strongly pH responsive over all accessible aqueous pH values.<sup>[137]</sup> The composite exhibited high capacitance and improved conductivity in acidic conditions compared to poor conductivity and insignificant capacitance in alkaline media. The deposition volume results in different film thicknesses and active surface areas. If the deposited carbon nanoparticles have good conductivity, then there should be an increase in the capacitive current proportional to the deposition volume, as demonstrated by Xia and coworkers. This study reported a completely electrochemically active core-shell film with a specific capacitance of 18 F g<sup>-1</sup> and linear dependence was observed with increasing amounts of carbon added (**Error! Reference source not found.**).<sup>[137]</sup> In contrast, an earlier study by Xia et al. looked at the same material with a thicker shell composition.<sup>[138]</sup> This resulted in an electrochemically inactive material and as a result it was only the ITO capacitance that was observed.

The negatively charged Emperor 2000<sup>TM</sup> carbon nanoparticles have been used in the formation of a novel core-shell material via “hydrothermal wrapping” in a poly-(4-vinylpyridine) cationomer (P4VP). The core-shell nanocomposite material that had a thin shell (20-40 nm wrapped particle diameter) was water-insoluble but could readily be dispersed into ethanol for straight forward deposition onto electrodes.<sup>[139]</sup> The strongly pH-dependent properties of the material were shown by using zeta-potential

measurements, which indicated a point of zero charge (PZC) occurring at approximately pH 4.5 suggesting that the negative functional groups were dominating in the more alkaline range and positive functional groups are dominating in acidic conditions (Figure 13B). Also, X-ray photoelectron spectroscopy (XPS) data suggested the presence of carboxylate and pyridinium functional groups as negative and positive charge bearers, respectively, which was confirmed by using voltammetric measurements for adsorbed cations (methylene blue) and adsorbed anions (indigo carmine). The specific capacitance reached a maximum of  $13 \text{ Fg}^{-1}$  at the PZC (Figure 13A), which was proposed to be caused by conductivity effects within the nanoparticle shell (Figure 13C).



**Figure 13.** (A) Plot of capacitance as a function of pH showing that at approximately pH 5 there was a considerable increase in the capacitance to  $0.65 \text{ F}$  (the specific capacitance was calculated to be  $13 \text{ Fg}^{-1}$ ), (B) Zeta potential measurements in  $0.1 \text{ M}$  PBS for (i) Emperor 2000™ CNPs and (ii) for P4VP-wrapped carbon nanoparticles, and (C) schematic diagrams of core-shell nanoparticles at different pH values.<sup>[139]</sup>

This type of core-shell nanomaterial and similar functionalised materials could be

useful for future sensing applications. The proton-sensitivity function could be developed into a series of more selective response mechanisms, for example to detect analytes such as heavy metals, pollutants, glucose, or trace bio-markers. Further possible synthetic methodologies to prepare highly functionalised materials could involve the post-hydrothermal synthetic modification of the shell or the impregnation of redox systems into the shell.

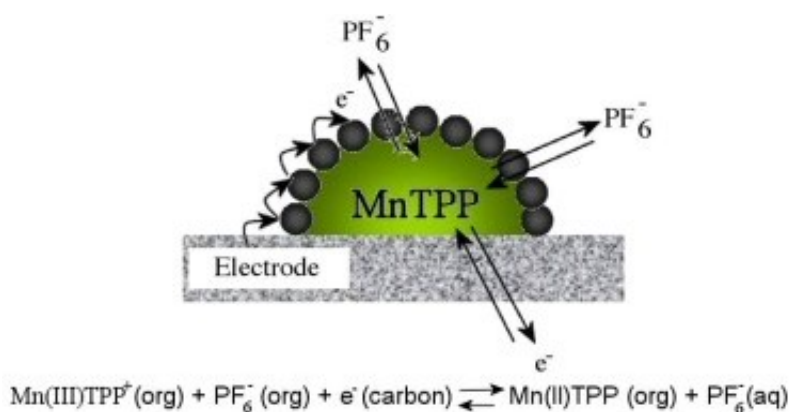
#### **4. Electrode Surfaces Modified with Carbon Nanoparticle**

##### **Composites**

Carbon nanoparticles can be adhered to a number of different working electrodes including glassy carbon, graphite, tin-doped indium oxide (ITO) etc. by using drop-cast or sol-gel<sup>[140]</sup> methodologies. Nanoparticles are commonly prepared as suspensions in ethanol, water, and other solvents.<sup>[141,142]</sup> This allows a drop to be placed directly onto the working electrode and evaporated to form either a continuous film or a layer of discrete nanoparticles, depending on the concentration of the solution and the drying process. If the chemical composition of the carbon nanoparticles and the deposition solvent allow, then this can form an insoluble film that allows for electrochemical analysis and characterisation.

Carbon nanoparticles have been shown to successfully catalyse simultaneous electron transfer and ion transfer processes at triple phase boundary interfaces.<sup>[143]</sup> CNPs have been used for a number of decades to stabilise liquid|liquid interfaces with high

binding constants and stabilising effects.<sup>[144,145,146]</sup> Unlike conventional surfactants, CNPs act as nanoparticle surfactants that create triple-phase boundary zones with space between the individual particles where interesting chemical and electrochemical reactions can occur through the liquid|liquid interface. In 2007, MacDonald and co-workers<sup>[147]</sup> studied microdroplets of a two-phase mixture that contained a redox active species, these resulting microdroplets were stabilised by using CNPs, and then immobilised on ITO electrode surfaces (Figure 14). The modified electrodes showed good electrochemical responses and the CNPs were thought to act in two ways: to stabilise the liquid|liquid interface and to provide additional active interfacial electron channels. This provided a novel way to probe ion-transfer reactions in organic oils at ITO electrodes, and for the development of ion-transfer sensors.<sup>[147]</sup>



**Figure 14.** Schematic representation of the interaction of a CNP stabilised microdroplet with an ITO electrode surface based on 5,10,15,20-tetraphenyl-21H,23H-porphinato manganese(III) chloride (MnTPP) undergoing a one electron reduction at surface-bound CNP, upon reduction  $\text{PF}_6^-$  is transferred from the organic phase to the surrounding aqueous phase.<sup>[147]</sup>

Nanocomposites of carbon with silica particles have been proposed for selective dopamine detection<sup>[148]</sup> where interfering processes are suppressed. A nano-composite with copper sulphide has been reported for direct methanol fuel cell applications.<sup>[149]</sup> Very interesting also is the development of CNP-graphene mixed-carbon composites

for a more stable performance of catalysts in fuel cells.<sup>[150]</sup> The choice of graphene to CNP ratio allows pore size and diffusion processes to be optimised whilst maintaining good electrical properties.

It has been pointed out that the charge of building blocks, e.g. carbon nanoparticles, can be used in layer-by-layer processes to form stable assemblies on electrode surfaces.<sup>[151,152]</sup> The presence of both positively and negatively charged surfaces in a “host composite” can be beneficial for the immobilisation and reactivity of enzymes and therefore applications of carbon nanoparticle building blocks in particular in bio-electrochemistry are of interest.

For bio-electrochemical systems, the reaction environment for biological catalysts and the direct transfer of electron via “conduits” are important. Activated carbon<sup>[153]</sup> and nano-carbons<sup>[154]</sup> are often employed to provide composite host environments in particular for enzyme. Carbon nanoparticles with negatively charged sulfonate functionalization embedded in a composite have been reported to support bilirubin oxidase based oxygen reduction.<sup>[155,156]</sup> Several redox protein and enzyme redox systems have recently been shown to be active when immobilised into mixed carbon nanoparticle hosts.<sup>[157]</sup>

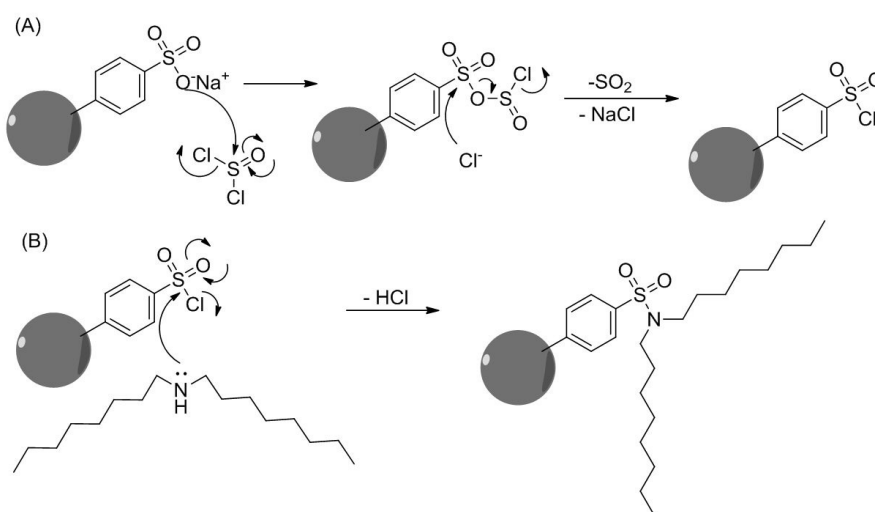
Emperor 2000<sup>TM</sup> CNPs have been the focus of a number of bioelectrocatalytic studies. Both Szot<sup>[158,159]</sup> and later Jensen<sup>[160]</sup> have used Emperor 2000<sup>TM</sup> carbon nanoparticles to create modified electrode surfaces to probe the direct electron transfer



communication between the electrode and *Cerrena* laccase enzymes for the bioelectrocatalytic reduction of O<sub>2</sub> to water. Direct electron transfer can be advantageous with respect to mediated enzymatic electrodes as the complexity is reduced, also toxicity and stability issues can be avoided.<sup>[161,162]</sup> However, many direct mechanisms have problems associated with low amounts of the enzyme being accessible because of poor orientation, which is required for direct electron transfer to occur. One approach to overcome these drawbacks is to introduce a high surface area electrode material such as carbon nanoparticles; this not only provides an increased surface concentration of the active enzyme but can also stabilise the enzymes.<sup>[163]</sup> Szot and co-workers prepared films containing Emperor 2000<sup>TM</sup> CNPs and laccase from *Cerrena unicolor* in a sol-gel matrix on ITO electrodes. To achieve successful enzyme orientation for electron transfer to occur between the CNPs and the enzyme active site, the laccase was mixed with a solution of CNPs in water to allow the enzymes to adsorb onto the carbonaceous surface. In contrast, Jensen et al. produced a bio-composite through entrapment of CNPs within a *Cerrena maxima* laccase-polymer matrix. The sulfonate modification of the carbon nanoparticles results in preferable orientation of the enzyme compared with the immobilisation of the enzyme on hydrophobic unmodified carbon black. This could be attributed to a more favourable electron transfer possible between the Emperor 2000<sup>TM</sup> nanoparticles with a hydrophilic nature and the hydrophilic enzyme surface. Both Szot and Jensen successfully tested the electrode as a biocathode in a zinc-dioxygen biofuel cell, which provided large voltages from the combination of the low potential Zn/Zn<sup>2+</sup> anode and the high potential bioelectrocatalytic dioxygen reduction at the cathode.<sup>[164,165]</sup> Szot reported a maximum power density of 17.6 μW cm<sup>-2</sup> at 0.7 V for *Cerrena unicolor*-CNP bioelectrodes, whereas Jensen achieved a maximum power

density of  $160 \mu\text{W cm}^{-2}$  at  $0.5 \text{ V}$  for *Cerrena maxima*-CNP bioelectrodes. This research demonstrated promise for the development of simple and cost-effective CNP-based biocathodes for biofuel cells.

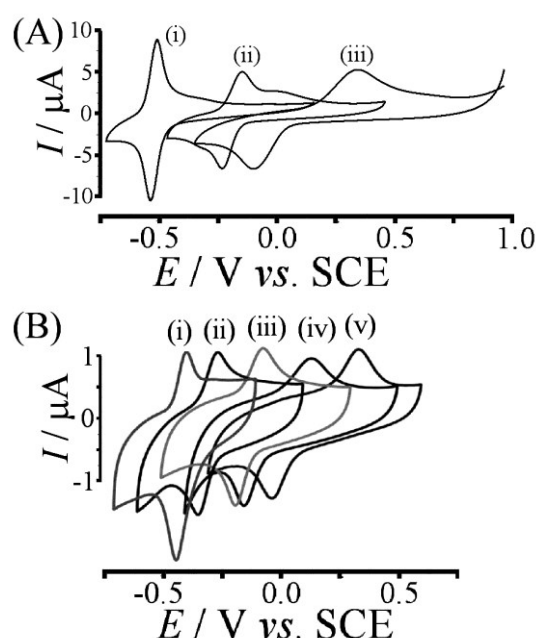
Covalent modification of Emperor 2000<sup>TM</sup> has enabled the synthesis of highly hydrophobic carbon black particles furnished with dioctylamine moieties (see Figure 15), which were compatible with lipid membranes.<sup>[166]</sup> These modified CNPs were employed as high surface area substrates to study coenzyme Q<sub>10</sub> and 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine-Q<sub>10</sub> (DMPC-Q<sub>10</sub>) redox processes. The modified CNPs provided a highly hydrophobic carbon substrate with a specific capacitance of approximately  $25 \text{ F g}^{-1}$  when no redox system had been added to the system. When coenzyme Q<sub>10</sub> or DMPC-Q<sub>10</sub> was immobilised onto the CNPs, the capacitance was lowered and therefore, resulted in well-defined voltammetric responses. The DMPC-Q<sub>10</sub> deposit showed very similar characteristics to those of pure coenzyme Q<sub>10</sub>, but with improved reproducibility and greater sensitivity.



**Figure 15.** (A) The reaction of the Emperor 2000<sup>TM</sup> carbon nanoparticles with thionyl chloride, and (B) the subsequent reaction between dioctylamine and the

chlorinated carbon nanoparticles.<sup>[165]</sup>

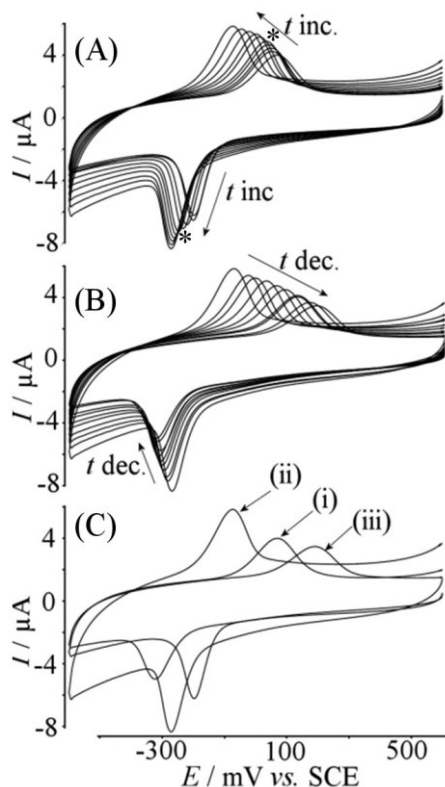
Enhanced voltammetric responses were observed, and in particular for the lipid film, high sensitivity with low levels of coenzyme Q<sub>10</sub> was achieved, which could be attributed to the suppression of the capacitive background current (Figure 16). The new hydrophobic CNP substrate was shown to be versatile and could be used to study both hydrophobic redox systems and lipid films.



**Figure 16.** Cyclic voltammograms (scan rate 10 mVs<sup>-1</sup>) for the reduction and back-oxidation of (A) 1 nmol Q<sub>10</sub> in 15 µg CNP immobilised at a glassy carbon electrode and immersed in aqueous 0.5 M PBS at pH (i) 12, (ii) 7, and (iii) 2; and (B) 0.1 nmol Q<sub>10</sub> in 25 nmol DMPC/15 µg CNP immobilised at a glassy carbon electrode and immersed in aqueous 0.5 M PBS at pH (i) 12, (ii) 10, (iii) 7, (iv) 5, and (v) 2.<sup>[165]</sup>

The effect of a phase transition within the lipid film is also detected directly by carbon nanoparticle voltammetry (Figure 17). The well-known gel-fluid transition point  $T_m = 23.8\text{ }^\circ\text{C}$  <sup>[167,168]</sup> is observed as an inflection in the development of the peak shape for

both anodic and cathodic signal (see the “\*” symbol in Figure 17 indicating the transition at ca. 25 °C). Upon cooling the system, no such inflection is observed consistent with a transition that occurs only during the heating-up stage.



**Figure 17.** (A) Cyclic voltammograms (scan rate of  $0.1 \text{ V s}^{-1}$ ) for CNP-DMPC-CoQ10 modified electrodes in 0.5 M phosphate buffer pH 7 recorded with increasing temperature from 10 °C to 55 °C in 5 °C steps. (B) As above with decreasing temperature. (C) Summary of data at (i) the starting temperature 10 °C, (ii) the maximum temperature 55 °C, and (iii) the final temperature 10 °C.<sup>[169]</sup>

In future, lipid-carbon nanoparticle film voltammetry could be beneficial for a wider range of lipid electroanalysis problems, for example (i) in the study of drug – lipid interactions, (ii) changes in phase transitions due to environmental factors, or (iii) for the analysis of complex biological lipid mixtures (containing fragile protein

complexes) and cell membranes transferred directly from living cells.

## 5. Summary and Outlook

Carbon nanoparticles and nano-dots represent important and broad families of electrochemically active materials. In contrast to carbon nano-materials such as fullerenes, graphene and carbon nanotubes, carbon nanoparticles are readily available or synthesised in bulk (using hydrothermal or combustion techniques), inexpensive, and relatively benign. Major directions in research for these materials currently are

- (i) making novel composites between different types of carbons or with other components (giving unusual materials with good electron transfer to redox proteins, higher fuel cell catalyst reactivity and stability, and improved energy storage systems),
- (ii) applying chemical treatments that lead to nano-scale chemical changes and associated with this dramatic changes in properties such as porosity, electrical conductivity, fluorescence, higher harmonic generation, and other optical properties (giving new classes of fluorophores and sensors as well as better solar cell components and supercapacitors), and
- (iii) surface functionalization via hydrothermal or direct chemical methods to introduce self-assembly functions, “smart” responsive mechanisms, or sensor receptors (giving novel composite materials for bioelectronics, medicinal tools, “Janus” particles, sensors, membranes, and nano-building

blocks for energy conversion).

Research in carbon nanoparticles is progressing rapidly and very basic and fundamental studies on properties and applications still need to be carried out. Uniformity and reproducibility in nanoscale materials will present a challenge and potential problems/new opportunities could emerge based on the biological activity and rate of degradation of carbon nanoparticles.

The focus here was the surface functionalisation which allows hydrophobicity/hydrophilicity, photo-electrochemical, and (bio-)electrochemical characteristics to be modified and redox systems/catalysts to be immobilised onto the extended carbon nanoparticle surface. In conjunction with proteins or lipid membranes composite “bio-carbon” systems are obtained with electrochemical control or with electricity generating functions (e.g. in biofilms). Future applications as nano-building blocks and conduits for electron transfer are widely feasible and exciting in particular for bio-electrochemical processes, energy applications, and in electroanalytical sensing.

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